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Electromechanical and dielectric properties of aluminium doped-barium titanate ceramics

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Cylindrical pellets of pure barium titanate as well as (0·05–0·3) wt.% aluminium doped barium titanate were prepared and sintered. Measurements of bulk density, dielectric constant, resonance mode frequency constant (KHZ.Cm) and Young's modulus (dyne/cm^2) were conducted on polarized and unpolarized specimens. Results indicated that, aluminium doping enhanced sintering at low temperature a case which would be at profit for industry

In this case, aluminium substitution in octahedral sites was most probable and increased the proportion of remnant 90° domain. At 0·1 wt.% aluminium doping, a constancy in the measured properties indicating best quality for ceramic dielectric, had been obtained

1. Introduction

In piezoelectric applications, barium titanate ceramics are used usually after polarization in a d c electric field of about 20 KV/cm In this poling process, domain orientations are altered and there remains the remenant polarization. Therefore, if 90° rotations of domains remain after the poling process, the dielectric constant of the polarized ceramics are expected to be very different from those of the unpolarized ones From this point of views, the anisotropy of polarized barium titanate ($BaTiO_3$) ceramics was studied in the tetragonal structure (Marutake 1957) It was shown that the 180° domains (reversals of domains) mainly remain after the poling process, and that anisotropy is due to piezoelectric interactions, among single crystals It was found that the addition of Al to lead zirconate-titanate enhanced sintering and decrease the grain size causing the increase of density of the modified lead zirconate-titanate (Atkin & Flurath 1971, Tawfik 1975). The dielectric constant of modified lead zirconate-titanate (PZT) containing aluminum additions increased with increasing of aluminium additions

The resonance frequency constant and the elastic properties of PZT ceramics exhibit pronounced decreasing as La is added to the lattice This behaviour is evidence for increasing ferro-elastic sensitivity of the material (Meitzler 1972) The properties of these materials, as function of La-doping, have been studied

in detail by electric and piezoelectric measurements (Haertling 1971, Land 1969, Carl 1970)

However, other attempts have been made by different authors (Berlin-Court 1955, Jaffe & Berlin-Court 1965) to show the effect of adding $PbTiO_3$ etc., on the electrical properties of $BaTiO_3$ fired at 1400°C They observed a decrease in the piezoelectric constants g_{31}, d_{31}.

The present work aim is to evaluate the dielectric and electromechanical properties of $BaTiO_3$ ceramic modified with a kind of additive that may be effective in producing a high piezoelectric response on firing at relatively low sintering temperature (1200°C) Low sintering temperature is economic for industry (at a profit) since it demands low cost of heat and cheap firing elements. This was made in continuation with other physical measurements (Amin & Tawfik 1972) which indicated that the piezoelectric response of $BaTiO_3$ containing 0·1 wt % Al and fired at 1200°C was higher than that of the same specimen fired at 1400°C and this was ascribed to the internal strain caused by the residual 90° domain after the poling process

2 Experimental Procedure

Barium titanate samples were prepared by dry mixing of equimolecular proportion of $BaCO_3$ and TiO_2 followed by firing at 1450°C and grinding The desired quantities of Al ranging from 0·0–0·3 wt % were added to the barium titanate powder and well mixed Final reaction and densification were achieved by firing of pressed pellets at 1200°C for 6 hours in an electric muffle furnace To achieve good contact, the two opposite surfaces of each pellet had been silvered. The sample dimensions were 15 mm diameter and one mm thickness.

The unmodified and modified $BaTiO_3$ containing up to 0·3 wt % Al were polarized by applying 2 KV/cm on the sample faces at its curie temperature. For this purpose, the samples were immersed in silicon oil and after cooling the field was removed

The dielectric constant of the polarized $BaTiO_3$ and $BaTiO_3$ containing up to 0·3 wt % Al was measured The temperature dependence of the dielectric constant was conducted up to 140°C on $BaTiO_3$ and 0·1 wt % Al-doped $BaTiO_3$

For measuring the resonance frequency and Young's modulus a signal generator and oscilliscope (Tawfik 1974) were employed The Young's modulus was calculated for each composition using the formula (Haertling 1971, Meitzler 1972)

$$Y = \frac{\pi^2 d^2 f_r^2 (1-\sigma^E)\rho}{\eta}$$

where Y = Young's modulus

f_r = resonance frequency of the tablet (C/S)

d = tablet diameter (cm)

ρ = density (gm/cm^3)

For σ^E = 0·31 Poisson's ratio (η_1)−2·05.

The change of η_0 and σ^E is negligible for the range of σ^E found in these ceramics.

3 Results and Discussion

Figure 1 indicates the effect of Al additions on the dielectric constant of $BaTiO_3$ specimens The observed high dielectric constant of $BaTiO_3$ containing 0·1 wt % Al was attributed to a rather more solid state interaction that takes

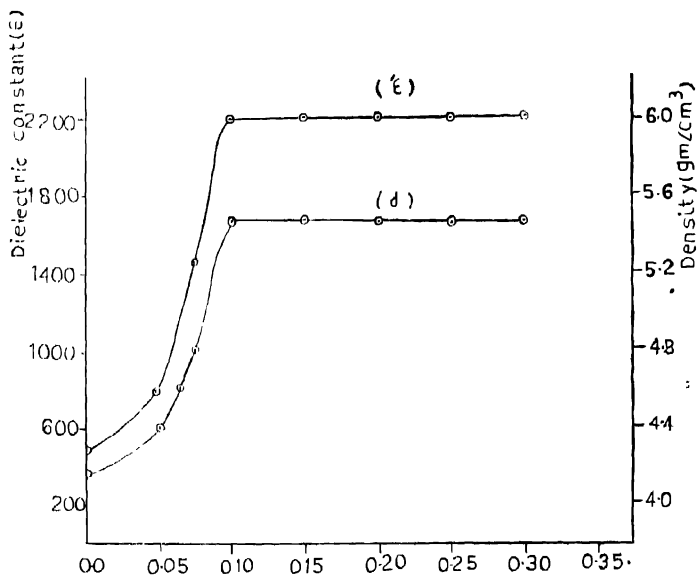

Fig. 1

place in the material This is indicated from the pronounced increase of density with the addition of Al. Doping with Al keeps the grain size small and thereby expedites densifications, therefore, it is more effective in accelerating sinterging. As was early shown (Atkin 1971) that the modified lead zirconate-titanate containing Al additives expedites densification at relatively low sintering temperature (1200°C). The increase of density of the sample beside the point defect

are due to substitution of Ti^{4+} by Al^{3+}. Accordingly, the electric charges are more loosely bound within the molecular structure in the modified $BaTiO_3$ causing an increase of its dielectric constant The previous explanation accord with a previous finding of Merz & Caspari (1950) on studying the dielectric constant of a perfect and defected crystals.

The temperature dependence of dielectric constant of the different barium titanate specimens are represented in figure 2. It is to be noted that, the peak value of dielectric constant was found at the curie temperatures (120°, 110°C)

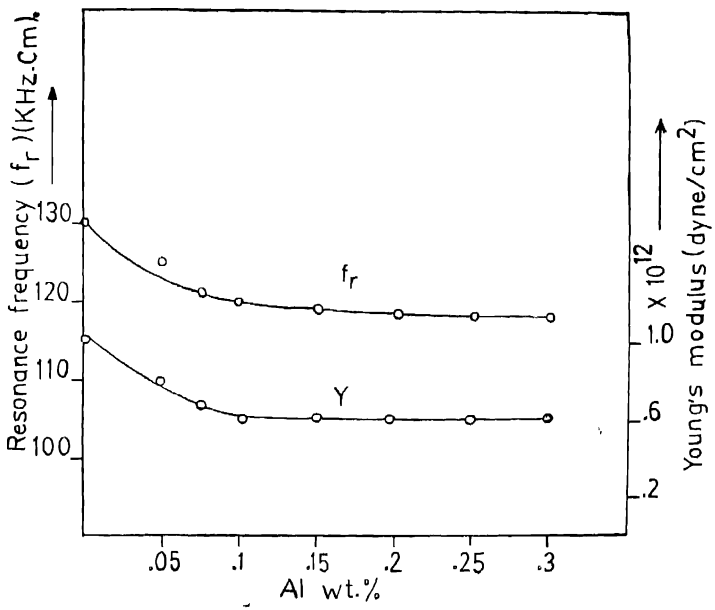

Fig. 2

for $BaTiO_3$ and 0·1 wt % Al modified $BaTiO_3$ specimens respectively This may be explained by the transition of crystal structure from tetragonal to cubic phase as previously obtained (Auluck 1972). The shift of curie point by lower temperatrre for $BaTiO_3$ containing 0·1 wt % Al, due to substitution of Ti^{4+} by Al^{3+}, is caused by the existence of lattice strain. In each case, the dielectric constant is decreased after polarization of samples. The percentage of anisotropy of the polarized $BaTiO_3$ and $BaTiO_3$ containing 0·1 wt % Al are 12% and 20% respectively. This can be discussed by the higher remained proportion of 90°

domain in the modified specimen and hence its more lattice strain. At the curie point the dielectric constant is the same for the polarized and unpolarized specimens due to the absence of polarization at this point.

The addition of Al to $BaTiO_3$ decreased the resonance frequency and Young's modulus as shown in figure 3. Barium titanate has a perovskite crystal structure with Ti^{4+} (ionic radius 0·68°A) Trivalent Al (0·51 A) is undoubtedly too

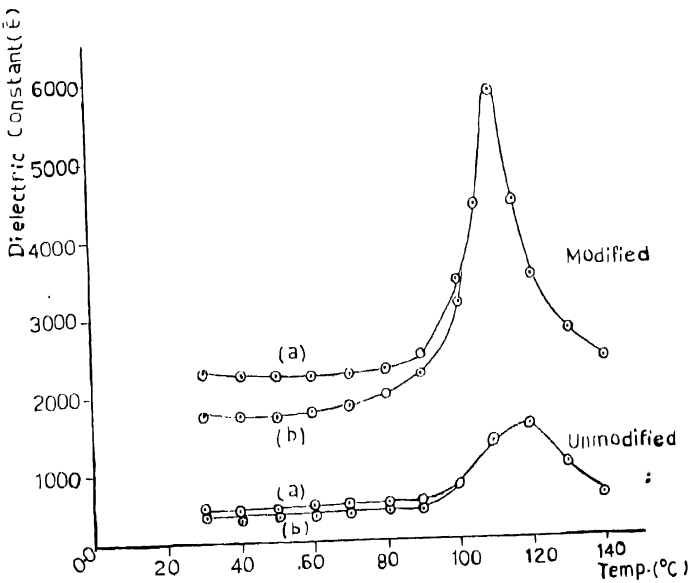

Fig. 2

large to enter interstitally and too small to replace Ba^{2+} so that substitution in octahedral sites is most probable However, the size and valence differences should tend to limit this substitution Weston *et al* (1969) found that Fe^{3+} (0·6°A) enters octahedral sites in PZT and that the solubility limit is 0·8 wt % Fe_2O_3

In this investigation, the electromechanical and dielectric saturation states (constancy) are attained at 0·1 wt % Al addition Thus, the 0·1 wt % Al addition may represent the solubility limit of Al in $BaTiO_3$ lattice

From the above results, it is clear that Al addition may increase the proportion of remenant 90° domain and the induced lattice strain. Thus, an easier

domain wall motion is attained This may result in an earlier disc vibration and hence a lower values of Young's modulus are obtained

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